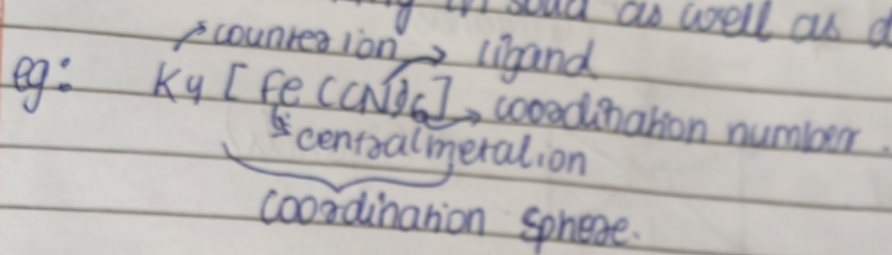


COORDINATION COMPOUNDS:

Coordination compounds are molecules which are formed by the combination of two or more stable compounds which retain their identity in solid as well as dissolved salt.



Central metal atom: electron acceptor which acts as a Lewis acid, mostly d block elements as they have vacant d orbitals.

Ligands: electron ~~acceptor~~ donor acts as a Lewis base, attached to the CMA through coordinate bonds, which gives electron to the CMA. Ligands can be ~~anionic~~ anionic, neutral or cationic molecules.

Coordination number: Number of donor atoms of the ligand which are directly bonded to CMA.

WIERNER'S THEORY:

Postulates; Werner stated that there are two types of valencies.

① PRIMARY VALENCY:- → are ionisable

$[CMA]$

→ satisfied by anions

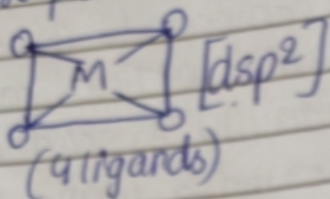
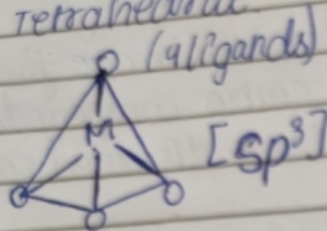
→ equal to oxidation number.

② SECONDARY VALENCY:- → non ionisable.

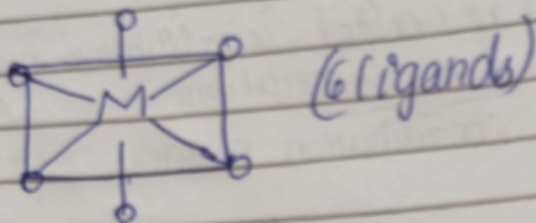
→ satisfied with ligands

→ equal to the coordination number.

- Coordination compounds have their own arrangements
- Tetrahedral (4 ligands)
 - Square planar



- Octahedral
- d^2sp^3 sp^3d^2



Double salts are formed from the combination of two or more simple stable compounds and dissociates completely when dissolved in water (ionisable).

Homoleptic complex:- CMA is bonded to one type of ligand. eg, $K_4[Fe(CN)_6]$.

Heteroleptic complex:- CMA is bonded to more than one type of ligand. eg, $[CoCl_3(NH_3)_5]$

~~Donor~~ Denticity: Number of lone pairs donated to the CMA by the ligand.

TYPES OF LIGANDS:-

- ① monodentate / unidentate ligands $\rightarrow$ one lone pair is donated to the CMA by the ligand.

Types of monodentate ligands

(a) Neutral ligands -

NH_3 - ammine
 H_2O - aqua
 NO - nitrosyl
 PH_3 - phosphine
 PPH_3 - triphenyl phosphine
 O_2 - dioxygen
 N_2 - dinitrogen
 CH_3OH - methyl alcohol
 CH_3NH_2 - methyl ammine
 NH_2CONH_2 - urea
 $\text{CH}_3\text{-O-CH}_3$ - dimethyl ether
 CO - carbonyl
 CS - thiocarbonyl
 NH_2NH_2 - hydrazine
 en - ethylenediamine
 $[\text{CH}_2\text{NH}_2]_2$

(b) Negative ligands -

F^- - fluoro
 Cl^- - chloro
 Br^- - bromo
 I^- - iodo
 N^{3-} - nitrido
 N_3^- - azido
 NO_2^- - nitro
 NO_2 - nitro - N, ONO - nitro - O
 NH_2^- - amido
 NH^- - imido
 OH^- - hydroxo, H^- - hydrido
 SCN^- - thiocyanato - S
 NCS^- - thiocyanato - N
 CN^- - cyano
 $\text{C}_2\text{O}_4^{2-}$ - oxalato (ox) [-2]
 CO_3^{2-} - carbonate
 $\text{S}_2\text{O}_3^{2-}$ - thiosulphato
 CH_3COO^- - acetato
 O^{2-} - oxo [polydentate]
 EDTA^{4-} - ethylenediaminetetraacetato [-4]

(2)

Bidentate ligands:- ligands which donate two lone pairs to CMA.

eg: $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$ oxalic acid

$\begin{array}{c} \text{CH}_2\text{-NH}_2 \\ | \\ \text{CH}_2\text{-NH}_2 \end{array}$ ethylenediamine (en)

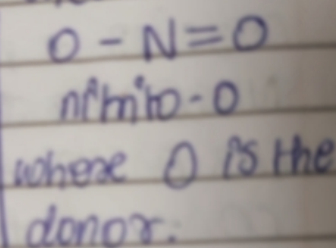
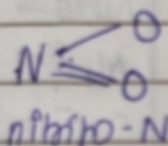
[ALL BIDENTATE LIGANDS ARE CHELATING LIGANDS]

* Chelating ligands: when ligands form coordinate bonds leading to cage like structures.
 NOT ALL CHELATING LIGANDS ARE BIDENTATE.

③ Polydentate ligands: more than two donor lone pairs are given to the CMA by a ligand.
 eg: EDTA, ethylenediamine tetraacetate.

* Ambident ligands: monodentate ligands which can coordinate with CMA through more than one site.

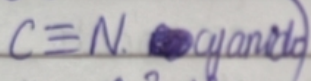
eg: ① $[NiO_2]$



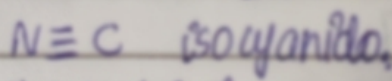
where N is the donor atom

either N or O can be the donor but not both.

② $[CN]$ either C or N can be donor but not both.



where C is the donor atom.



where N is the donor.

Coordination Number: total number of ligands attached to the CMA through coordinate bonds.

ISOMERISM: two or more coordination compounds having same molecular formula but different structural formula.

STRUCTURAL ISOMERISM

→ Ionisation isomerism → switching countable ions.
if these ions are outside the coordination sphere.
• say $\rightarrow$ white ppt with BaCl_2
• $\text{Br}^- \rightarrow$ pale yellow ppt with AgNO_3

→ Hydrate isomerism → molecules have different numbers of water molecules and water of hydration.

→ if one Cl is outside $\rightarrow$ bright green
→ if two Cl [Cl_2] is outside $\rightarrow$ grey green
→ if three Cl [Cl_3] are outside $\rightarrow$ violet

→ Coordination isomerism → interchange ligands

→ Linkage isomerism → two different donor atoms.

eg: $\text{ONO} \rightarrow$ red
 $\text{NO}_2 \rightarrow$ yellow.

STEREISOMERISM:-

→ Geometrical isomerism → different spatial arrangement but same molecular/structural formula.

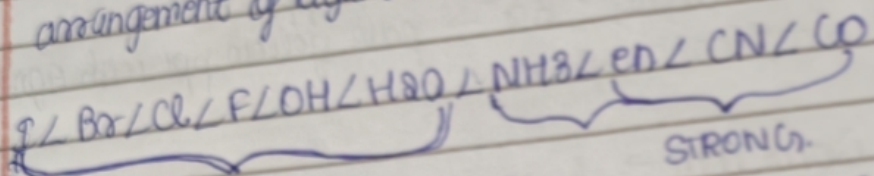
same side $\rightarrow$ CIS, CIS isomers are optically active
different side $\rightarrow$ TRANS, TRANS isomers are optically inactive

→ OPTICAL isomerism → • In chiral form
• forms non super imposable images.

[Tetrahedral, square planar do not show geometrical]

★ Valence Bond Theory [VBT]
 formation of coordination complex due to the overlapping
 of metal vacant d orbitals.

arrangement of ligands in their increasing strength.



no pairing of e⁻s.

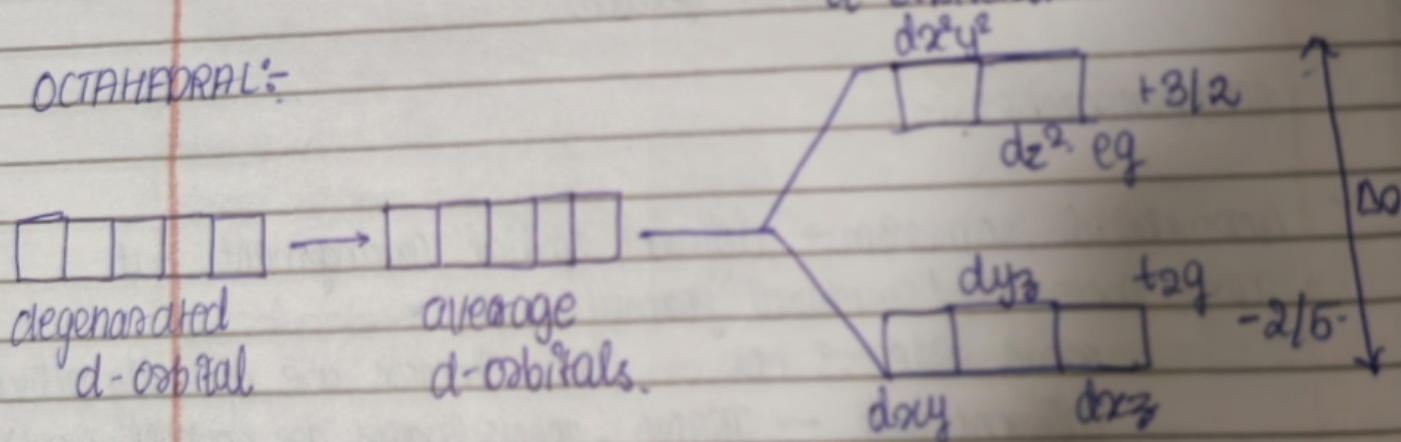
pairing of e⁻s.

Limitations of VBT →

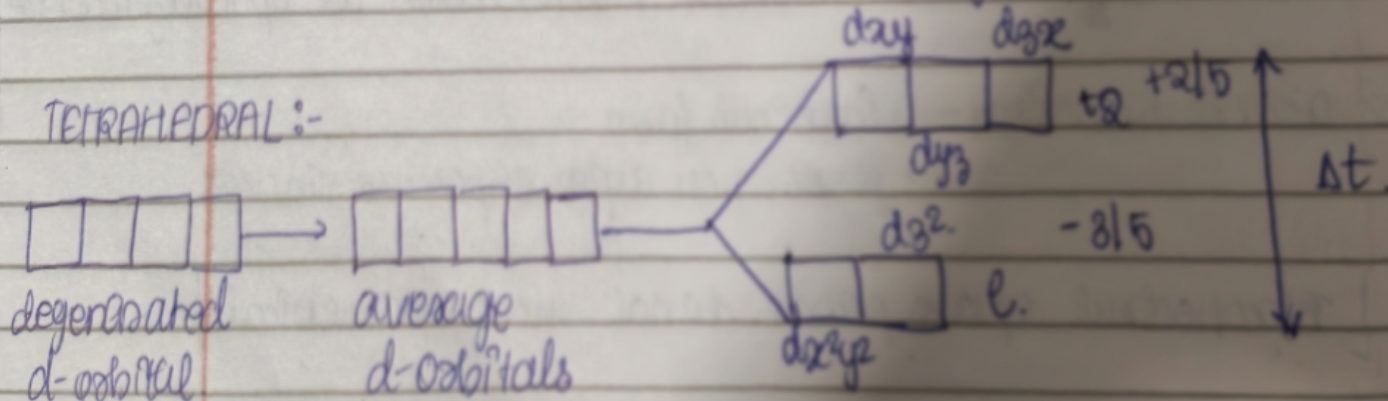
- does not explain colour exhibited by coordination compounds
- It does not distinguish b/w strong & weak field ligands.

CRYSTAL FIELD THEORY [CFT]: splitting of metals of d-orbitals.

OCTAHEDRAL:-



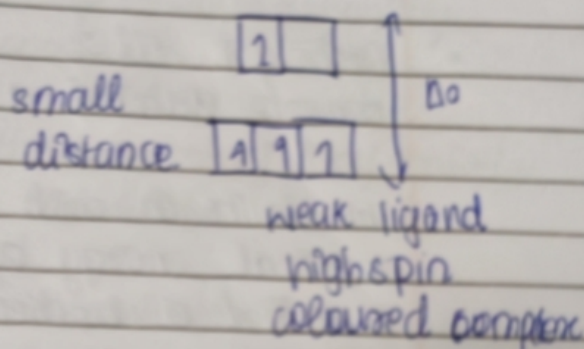
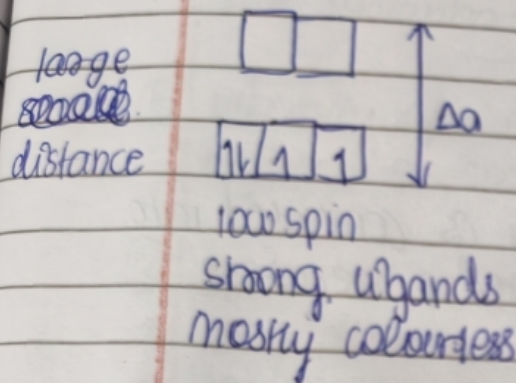
TETRAHEDRAL:-



The difference in energy b/w e_g and t_{2g} is known as CFSE.

* on basis of CFT write electronic configuration of d^4 in terms of t_{2g} and e_g in octahedral.

(a) $\Delta_o > P$: forced pairing



→ Tetrahedral complexes do not show geometrical isomerism and only form of (abcd) show optical isomerism.

→ square planar (dsp^2) show no optical isomers show
 $abcd \rightarrow 3$ geometrical
 $aabc \rightarrow 2$ geometrical
 $aab_2 \rightarrow 2$ geometrical

EC depends on magnitude of Δ_o and pairing energy depends on nature of ligands.

IMP Questions:-

- NH_3 is a strong ligand but in case of $[Co(NH_3)_6]^{3+}$ NH_3 acts as a weak ligand.
- $CoCl_3 \cdot 6H_2O$ gave 1 mole of $AgCl \rightarrow [CoCl_2(H_2O)_4] \cdot 2H_2O$
eg: $[CoCl_3(H_2O)_3]$ will not form precipitate with $AgNO_3$ as no ions are present outside the coordination sphere to react with it.

ELECTROCHEMISTRY:

- Electrochemical cell / galvanic / voltaic cell :
converts chemical $\rightarrow$ electrical

- Electrolytic cell :
converts electrical $\rightarrow$ chemical

The device in which chemical energy is converted into electrical energy by spontaneous redox reaction is called electrochemical cell.

Metalllic conduction

- physical changes occur
- electrons carry current
- in solid state
- conductivity $\downarrow$, temp $\uparrow$

Electrolytic conduction

- chemical changes occur
- Ions carry current
- In molten or aqueous
- temp $\uparrow$, conductivity $\downarrow$

$\rightarrow$ electrolytes allow the passage of electricity through them in molten or aqueous soln state.

$\rightarrow$ Strong electrolytes : dissociates completely into ions in soln. $\alpha = 1$.

eg: All strong acids, strong bases and salts
 NaCl , NaOH , H_2SO_4 .

$\rightarrow$ Weak electrolytes : partially dissociate into ions in solns. $\alpha < 1$. eg: weak acids, weak bases.

NH_4OH , NH_4Cl

$\rightarrow$ Non electrolytes : ~~partially~~ substances which do not conduct in solns. non polar covalent compounds are non electrolytes.

Factors affecting electrolytic conduction:

- ① Nature of electrolyte →
 - Strong electrolyte: high conduction.
 - Weak electrolyte: low conduction.
- ② Solvation of ions →
 - more solvation → bigger effective size → lower mobility
 - hence lower conduction
- ③ Viscosity of the solns:
 - higher the viscosity → slower the movement of ions/particles
 - hence lower conduction.
- ④ Concentration of soln:
 - very dilute → fewer ions → low conduction
 - moderate → ~~more~~ more conduction.
 - very concentration → ion pairing → higher conduction.
- ⑤ Nature of solvent:
 - polar solvents have stabilized ions → high conduction
 - non polar solvents have poor conduction.
- ⑥ Temperature → high temperature → more mobility → higher conduction

• $R = \rho \frac{l}{A}$, ρ = specific resistance / resistivity

• conductance [G or C]

$$G = \frac{1}{R} \Rightarrow \boxed{G = \frac{k \cdot A}{l}}$$

→ conductivity of unit volume of electrolyte soln.
 • Conductivity (K)
 $K = \frac{1}{\rho}$

→ $k = \text{conductivity} \mid \text{specific conductance}$
 → $K = \Omega / m$

★ conductivity decreases upon dilution.

• cell constant → [G*] It is the ratio of length of electrode to the area of cross section of the electrode

$$G^* = \frac{l}{A} \quad \text{OR} \quad K = G \times G^*$$

→ Relation b/w G^∞ , R and K .
 G^∞ is cell const, R is resistance, K is conductivity

$$R \cdot K = G^\infty$$

$$R \cdot K = \frac{l}{A} \Rightarrow K = \frac{l}{A \cdot R}$$

$$\left[\begin{array}{l} K = G \times G^\infty \\ K = \frac{1}{R} \times \frac{l}{A} \\ K \cdot R = G^\infty \end{array} \right]$$

→ Molar conductance / conductivity [IS A BULB FACTOR] (χ_m)
 conductance due to all ions present in an electrolyte soln containing one mole of the electrolyte.

★ MOLAR CONDUCTIVITY INCREASES ON DILUTION

$$\lambda_m = \frac{K}{C} \Rightarrow \lambda_m = \frac{K \times 1000}{C}$$

specific conductance

SI unit $\rightarrow \text{scm}^2/\text{mol}$
OR $\Omega\text{m}^2/\text{mol}$

→ Equivalent Conductance (λ_{eq})
 conductance due to all ions present in a electrolytic soln containing one gram equivalent mass of the electrolyte.

$$\lambda_{eq} = \frac{1000 \cdot K}{N} \quad \text{SI unit} = \Omega\text{m}^2/\text{g eq.}$$

→ $N = \frac{\text{no. of gram eq.}}{\text{vol of soln.}}$

→ $\text{gram eq} = \frac{\text{wt of solute}}{\text{eq wt.}}$

→ $\text{eq wt} = \frac{\text{mol wt}}{\text{basicity / acidity / +ve valency of metals}}$

As dilution $\uparrow$, λ_m also increases, at infinite dilution, λ_m is maximum and is called limiting molar conductivity.

→ Kohlrausch's law: The molar conductivity at infinite dilution is equal to the sum of molar conductivities of its cations and anions which each conductance term multiplied by their stoichiometric coefficients.

α = degree of dissociation is the ratio of molar conductivity at infinite dilution.

① $\alpha = \frac{\lambda_m}{\lambda_m^\infty}$ ② $K = \frac{C\alpha^2}{1-\alpha}$ [dissociation constant]

$\lambda_m \rightarrow$ molar conductance

$\lambda_m^\infty \rightarrow$ molar conductance at infinite dilution.

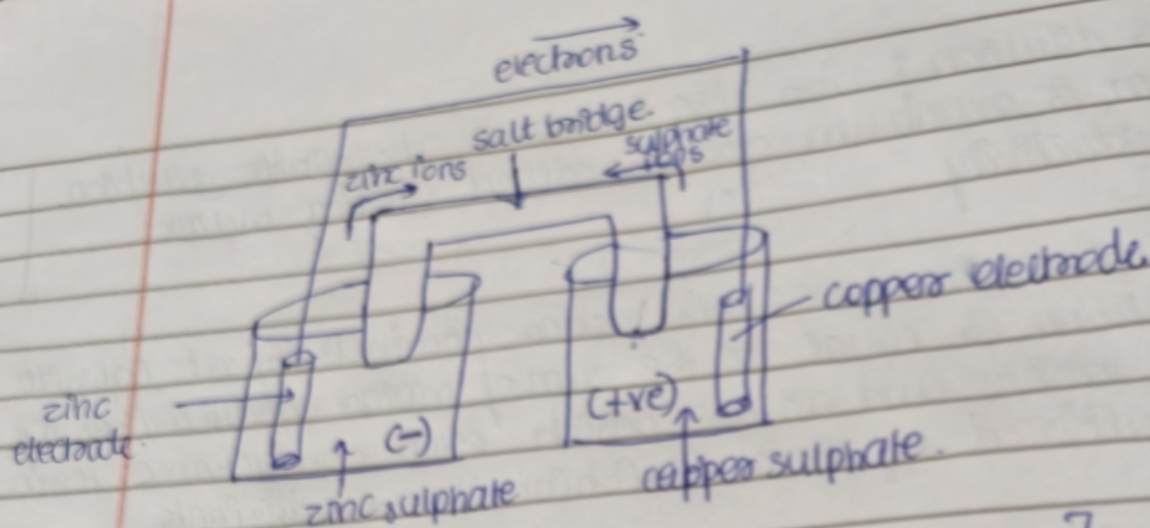
③ solubility of sparingly soluble salt = $\frac{K \times 1000}{\lambda_m^\infty}$

Electrochemical cells:-

- spontaneous redox reaction
- chemical $\rightarrow$ electrical
- $\Delta G = -ve$ eg: Daniel cell.

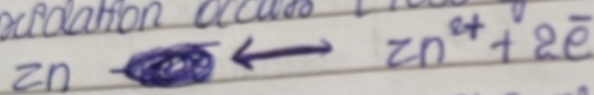
DANIEL CELL: A B C
 $\downarrow$ $\uparrow$ salt bridge
 anode cathode.





In a Daniell cell: [HALF CELL REACTION]

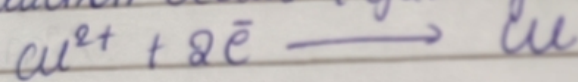
At anode: oxidation occurs [loss of e^-]



anode diminishes in mass

conc of Zn^{2+} ion increases.

At cathode: reduction occurs [gain of e^-]



cathode swells up in mass

conc Cu^{2+} decreases at cathode.

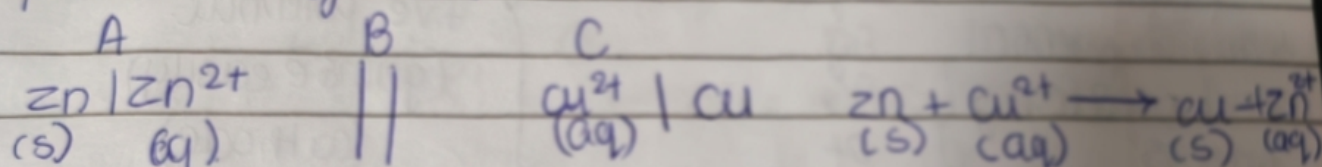
significance of salt bridge:

- made up of agar agar jelly stuffed in a hollow glass tube.
- The jelly contains KCl , KNO_3 .
- The ends of the glass tube is plugged with cotton to prevent electrolytes coming in contact with each other.

function of salt bridge:

- completes internal circuit
- maintains electrical neutrality - during reaction Zn^{2+} increase at anode, so there's a +ve charge at anode and -ve charge at cathode due to SO_4^{2-} . Thus reaction comes to stop. Cl^- ions are sent to anode and K^+ ions are sent to cathode which neutralises the excess charge.
- Ext voltage $< 1.1\text{V}$, operates as an Daniel cell.
- Ext voltage $= 1.1\text{V}$, no current flows
- Ext voltage $> 1.1\text{V}$, operates as an electrolytic cell.

Representation of cell:



- Electrode Potential: Tendency of an electrode to gain or lose electrons with a soln of its own when temp is 298K , conc of ions is 1 mol/dm^3 then the potential is referred to as standard electrode potential.
- spontaneous reaction: +ve cell
- non spontaneous reaction: -ve cell

Electrochemical series:- arrangement of elements in their increasing order of standard reduction potential.



Li
K
Na
Ca
Mg
Al
Zn
Fe
Pb
Sn

low reduction potential
{ good reducing agents }
higher oxidation potential

-ve potential
(loses e^- easily)
(anode)

H
Cu
Ag
Au
Pt

higher reduction potential
{ good oxidising agents }
lower oxidation potential

+ve potential
(gains e^- easily)
(cathode)

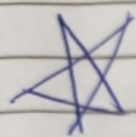
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

Factors affecting electrode potential -

- nature of metal & ions,
- conc of ions in soln,
conc $\uparrow$, reduction potential $\uparrow$
conc $\uparrow$, electrode potential $\downarrow$

NERNST EQUATION:-

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{anode}]}{[\text{cathode}]}$$



If temp is 298K or 25°C.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{anode}]}{[\text{cathode}]}$$

EMF is +ve $\rightarrow$ Spontaneous Reaction.

EMF is -ve $\rightarrow$ Non Spontaneous Reaction.

SHE:- standard electrode potential which is used as a reference electrode potential of other cells.

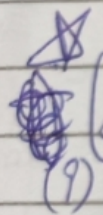
In SHE $E^{\circ}_{\text{ion}} = 0$.

$$\rightarrow \Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} \quad \rightarrow \Delta G = -nFE_{\text{cell}}$$

equilibrium $\rightarrow E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log K$

$$\log K \rightarrow K = \frac{[\text{anode}]}{[\text{cathode}]}$$

$$\rightarrow \Delta G^{\circ} = -2.303RT \log K$$



(9) Faraday's laws of electrolysis.

Faraday's 1st law:- The mass of substance deposited at an electrode during electrolysis is directly proportional to the quantity of electricity passed.

$$W \propto Q$$

$$W \propto It$$

$$W = ZIt$$

$$Z = \frac{M}{nF}$$

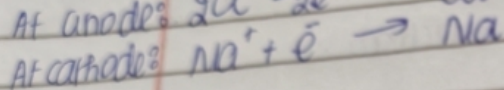
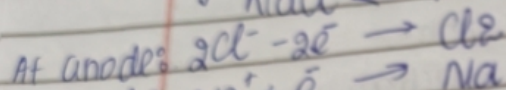
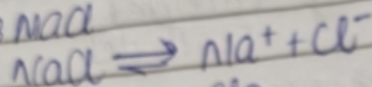
$$\text{Soln} = \frac{MIt}{nF}$$

Def of ece:- mass of substance deposited at an electrode when 1A current flows through an electrolyte for a sec.
unit $\rightarrow$ kg/coulomb.

(ii) Faraday's second law: During electrolysis the mass of a substance deposited at the electrode is directly proportional to their chemical equivalent mass.

$$W_1 \propto F \Rightarrow \frac{W_1}{W_2} = \frac{F_1}{F_2}$$

eg: NaCl



1 mole of e^- = deposits 1 mole of Na $\Rightarrow 1F = 96500C$

2 mole of e^- = deposits $\frac{1}{2}$ mole of Cl $\rightarrow \frac{1}{2}F = 48250C$

Batteries :- Arrangement of electrochemical cells which acts as a source of dc at constant voltage.

An ideal battery should be

- light and compact.
- has a long life
- should have constant voltage
- should not corrode.

Battery

(1) Primary

• Not rechargeable
(use & throw)

• Reactions cannot be reversed

eg: Leclanche cell, ✓
voltage cell, mercury cell. ✓

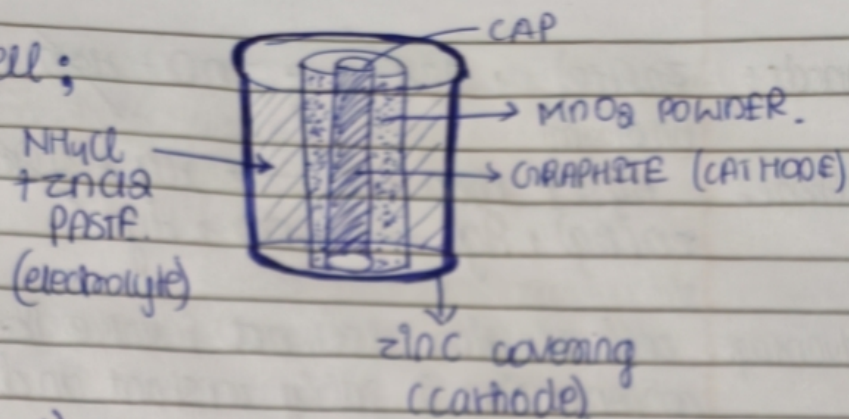
secondary (2)

• should be rechargeable

• can be reversed

eg: Ni-Cd cell, ✓
Pb-storage, ✓
battery.

(1) Leclanche cell;



At anode : Zn cylinder

At cathode : graphite (inert)

electrolyte: $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ paste.

MnO_2 powder surrounds the graphite cathode.

Anode: $\text{Zn} \rightarrow \text{Zn}^{2+}$

Cathode: $\text{NH}_4^+ + \text{MnO}_2 \rightarrow \text{MnO(OH)} + \text{NH}_3$

Overall: $\text{Zn} + 2\text{NH}_4^+ + 2\text{MnO}_2 \rightarrow \text{Zn}^{2+} + 2\text{MnO(OH)} + 2\text{NH}_3$

NH_3 formed combines with Zn^{2+} and Cl^- to form $\text{Zn(NH}_3)_2\text{Cl}_2$ which leads to cracking of seal due to pressure.

Voltage : 1.2 - 1.5V

Short life due to acidic conditions due to NH_4^+ ions.

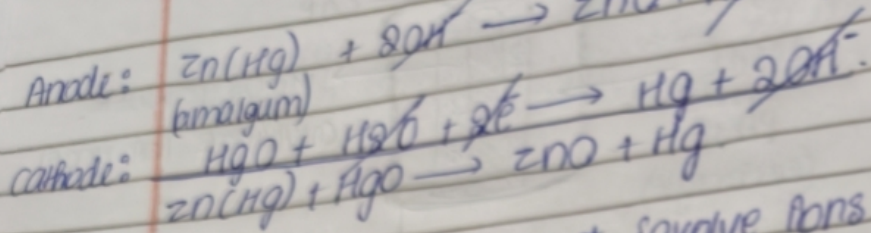
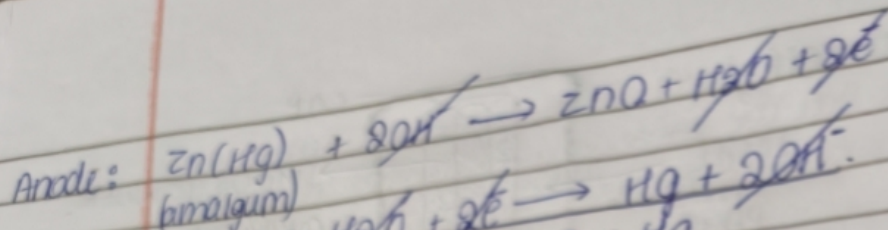
(1) (II)

Mercury cell : used in small gadgets like watches, hearing aids etc.

Anode: Zn

Cathode: HgO

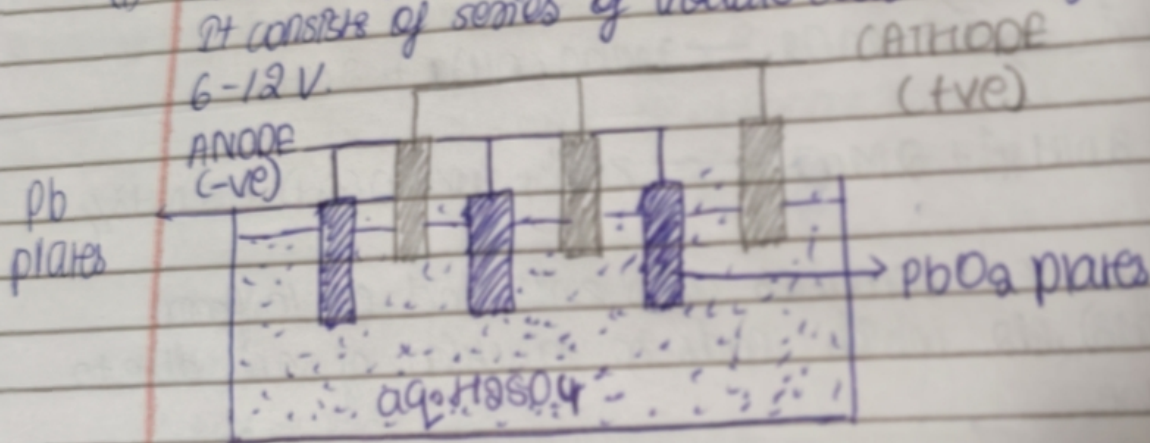
electrolyte: Paste of KOH and ZnO



Advantage: cell reaction does not involve ions hence concentration is fairly constant and so is voltage (1.35V)

(III) SECONDARY CELL:

(i) Lead storage battery:- Automobile batteries.
It consists of series of voltaic cells, voltage is 6-12 V.

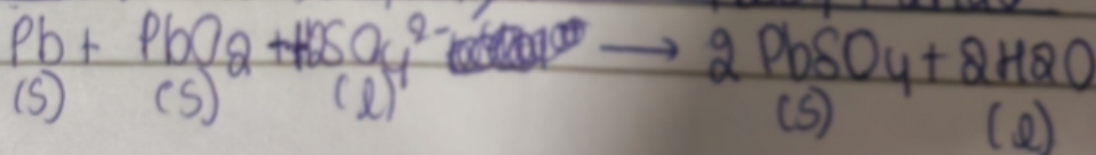
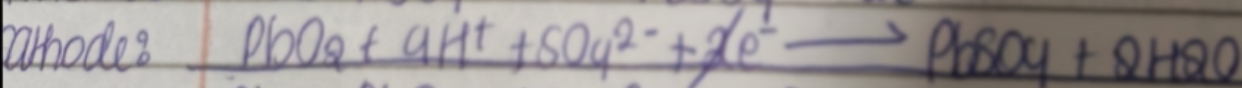
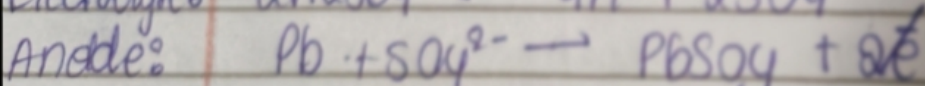
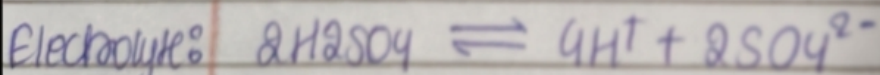


Anode: series of Pb packed with finely divided spongy lead.

Cathode: grid of PbO_2 plates

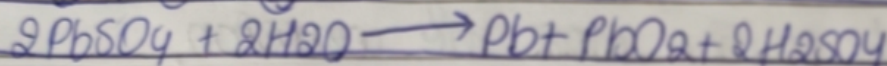
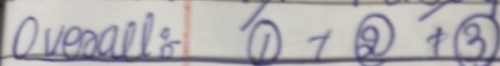
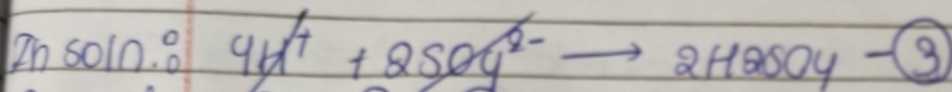
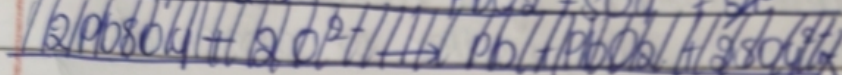
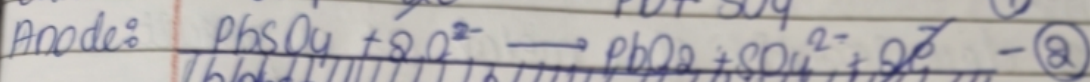
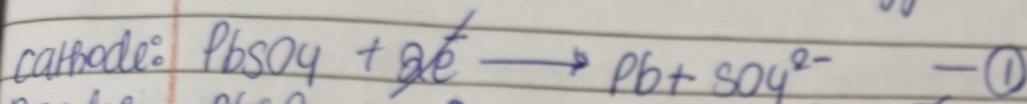
Electrolyte: 38% H_2SO_4 solution, sp. gravity 1.8 g/L

While using (It acts like electrochemical cell)



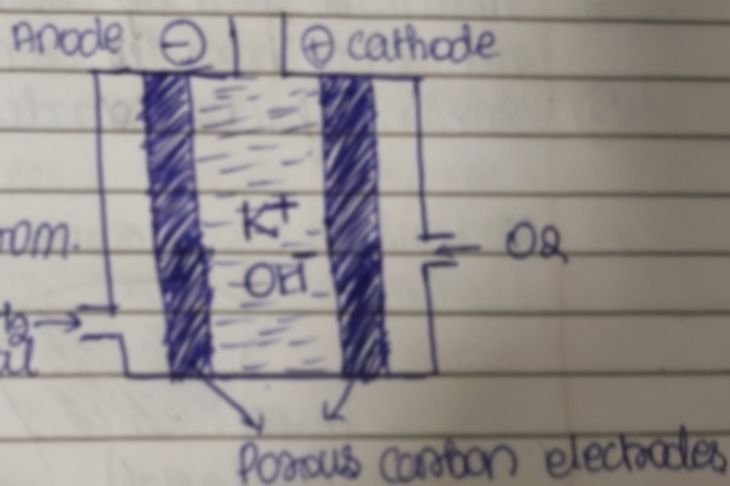
Potential of cell depends on conc H_2SO_4 . As a result of usage when conc falls below 1.2 g/l battery needs recharging.

While Recharging: It behaves like electrolytic cell. Electrical energy converts to chemical energy

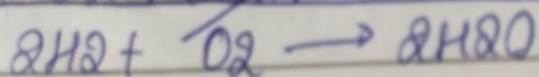
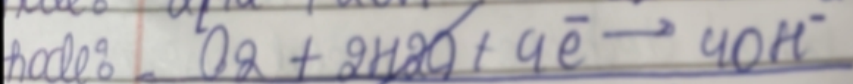
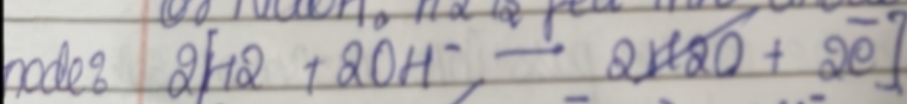


(ii) FUEL CELLS:

Voltage cells in which reactants are continuously supplied, converts energy from combustion of fuels such as H_2 , O_2 , CH_4 etc to electrical energy.



H_2 and O_2 are bubbled through porous carbon into conc KOH or NaOH . H_2 is fed into anode and O_2 to cathode



Used in Apollo space programme as the cell runs as long as H_2 and O_2 is fed.

Advantages:- High efficiency: 60-70% energy (conventional method are only 40%)

- Continuous source: No need to replace the electrodes.
- No pollution & only H_2O is the byproduct

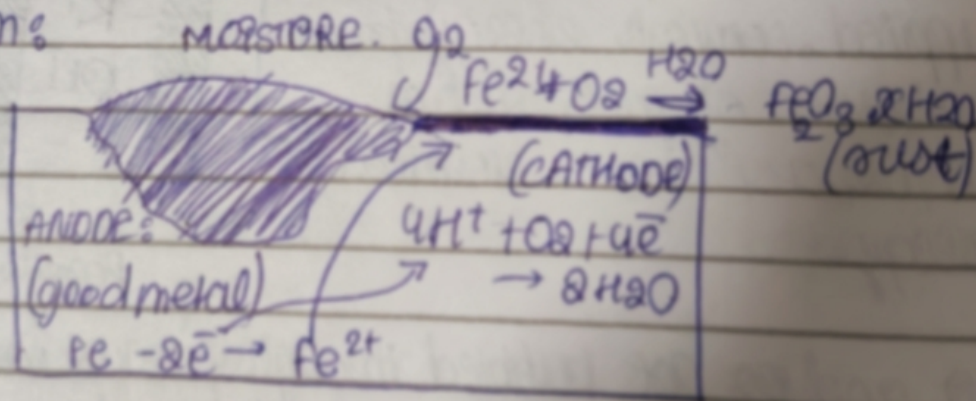
Corrosion:-

Process of deterioration of a metal as a result of its reaction with air, water or surrounding

Factors:-

- ① position of metals in reactivity series:
Higher the position, more the corrosion.
- ② Impurities speed up corrosion:
salt water corrodes iron faster.
- ③ Pressure of CO_2 corrodes the objects faster.

Mechanism:-



Anode: Metal atom in the lattice pass into moisture soln as Fe^{2+} ions; leaving behind electrons on metal surface

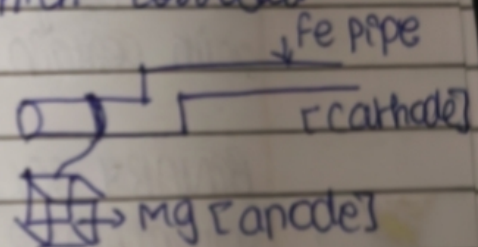
Cathode: The e^- migrate to various spots and react with atmospheric O_2 in presence of H^+ ions

Electrolyte: moisture with dissolved CO_2 acts as electrolyte.

~~Prevention~~ Prevention: • Barrier protection.
→ painting the surface
→ greasing or applying oil
→ electroplating with Sn, Cr, Ni etc

* Sacrificial protection:- • Fe is coated with more reactive metal like Zn (galvanisation), which undergoes corrosion in preference to iron.

* Electrical protection:- used in underground pipes, Fe pipes are connected to Mg block (or Zn) which corrodes.



* Anti Rust solutions:- Alkaline sodium phosphate or alkaline chromates

SOLUTIONS :-

Mixture $\rightarrow$ combination of two or more substances.

Homogeneous	Heterogeneous
• not distinct phase and is uniform throughout	• distinct layers & phases and is not uniform throughout.
eg: salt + water alcohol + water	eg: oil + water sand + water.

Solution: A homogeneous mixture with two or more non chemically reacting substance whose composition can be variable with certain units.

BINARY SOLUTIONS: has two components:-

- solvent (A): is in larger quantity, solute gets dissolved in it.
- solute (B): substance that's dissolved in solvent.

GASEOUS SOLUTIONS

LIQUID SOLUTIONS

SOLID SOLUTIONS

• GAS + GAS

eg: Air

• GAS + LIQUID

eg: water vapour.

• GAS + SOLID

eg: sublimation of camphor.

• LIQUID + GAS

eg: carbonated gas

• LIQUID + LIQUID

eg: water + alcohol

• LIQUID + SOLID

eg: salt + water

• SOLID + GAS

eg: accumulation of gas on metal surface: Adsorption

• SOLID + ~~SOLID~~ LIQUIDS

eg: amalgam

• SOLID + SOLID

eg: steel, brass.

solubility: maximum amount of solute that can be added to a solvent at a specified temperature.

concentration: amount of solute present per unit of a solvent or solution.

A = SOLVENT

B = SOLUTE

W $\rightarrow$ MASS

M $\rightarrow$ MOLAR MASS

(I) ~~Concentration Terms~~
Concentration Terms:-

(1) MASS PERCENT:

$$\rightarrow \text{mass percent of A} = \frac{W_A}{W_A + W_B} \times 100.$$

$$\rightarrow \text{mass percent of B} = \frac{W_B}{W_A + W_B} \times 100.$$

(2) VOLUME PERCENT:

$$\rightarrow \text{volume percent of A} = \frac{V_A}{V_A + V_B} \times 100.$$

$$\rightarrow \text{volume percent of B} = \frac{V_B}{V_A + V_B} \times 100.$$

(3) ~~Parts per million~~ (ppm)

$$\text{ppm} = \frac{\text{mass of component}}{\text{Total mass of soln}} \times 10^6$$

(4) Molarity (M): no of moles of solute in 1 litre soln.

$$\text{molarity} = \frac{n_B}{V} \times 1000 \quad \left[n_B = \frac{W_B}{M_B} \right]$$

$$M = \frac{W_B \times 1000}{M_B \times V(\text{ml})}$$

SI unit $\rightarrow$ mol/L.

Molarity depends on volume, which depends on temperature so molarity fluctuates, hence it is not ideal for calculation of concentration.

(5) Molality (m): no of moles of solute present in 1 kg of solution / solvent.

$$m = \frac{n_B \times 1000}{W_A}$$

$$m = \frac{M_B \times 1000}{W_B \times W_A}, \text{ unit} = \text{mol/kg}$$

Independent of volume and temperature hence is ideal for calculation of concentration.

(6) mole fraction: ratio of moles in one component to the total no of moles in the soln.

$$x_A = \frac{n_A}{n_A + n_B}$$

$$x_B = \frac{n_B}{n_A + n_B}$$

$$x_A + x_B = 1$$

$$n = \frac{W}{M}$$

no of moles

(7) Normality (N): no of gram equivalents of solute dissolved in one litre of solution.

$$N = \frac{\text{no. of gram equivalent}}{\text{vol of soln, in L}}$$

$$\text{gram equivalent} = \frac{\text{wt of solute}}{\text{Eq wt.}}$$

$$\text{Eq wt (acid)} = \frac{\text{mol wt}}{\text{basicity}}$$

$$\text{Eq wt (base)} = \frac{\text{mol wt}}{\text{acidity}}$$

$$\text{Eq wt (salt)} = \frac{\text{mol wt}}{\text{total +ve valency}}$$

(II) solubility of gases in liquids:

Factors affecting solubility;

(i) Nature of gases: gases which are liquefiable (apply pressure and they turn into liquids) are soluble. Every gas has a unique critical temperature beyond which cannot be liquefied.

★ Higher the critical point/temperature (T_c), easier to liquefy and more soluble in water.

(ii) Effect of temperature: when gases are dissolved in liquids heat is evolved, hence it's a ~~end~~ exothermic reaction. According to Le Chatelier's principle when temp is increased reaction proceeds in backward direction and gas tries to escape from the soln.

★ $\text{temp} \propto \frac{1}{\text{solubility}}$

(iii) Effect of pressure: [partial pressure (p) is pressure exerted by all the molecules on one gas.]

★ Henry's Law: According to this law at constant temperature the amount of gas dissolved in a liquid is directly proportional to partial pressure of the gas.

$$C \propto P$$

$$x \propto P$$

$$P = K_H x$$

$$\frac{P}{K_H} = x$$

$$x \propto \frac{1}{K_H}$$

C = conc, P = pressure

x = mole fraction

K_H = Henry's constant.

• mole fraction is inversely proportional to Henry's constant.

• Greater the K_H, lesser the solubility

• as temp ↑, K_H also increases

Application of Henry's Law:-

- ① Aquatic organisms are not comfortable in warm water: When the temp, solubility of O_2 ↓ ∴ breathing becomes difficult as O_2 is dissolved.
- ② Aerated drinks: CO_2 is kept pressurised in order to dissolve it in H_2O . When seal is broken, pressure decreases and CO_2 escapes.
- ③ Scuba diving: Deepsea divers depend on compressed gas for underwater diving which contains N_2 in addition to O_2 . As we know, N_2 is not soluble in blood under normal conditions, however it remains dissolved due to high water pressure, as the divers come back to the surface, pressure decreases and N_2 tries to rise up blocking capillaries. This is a painful situation called bends, now-a-days helium gas is used instead of N_2 .

(III) Liquid in liquid solutions:

$$P = P_A + P_B$$

$$P_A = P_A^\circ \cdot x_A$$

$$P_B = P_B^\circ \cdot x_B$$

P_A - partial pressure of A

P_A° - vapour pressure of solution

x_A - mole fraction of A.

P_B - partial pressure of B

P_B° - vapour pressure of solution

x_B - mole fraction of B.

★ Ideal solution: solution that obeys Raoult's law at all temperature and concentration.

$$A-A = B-B = A-B$$

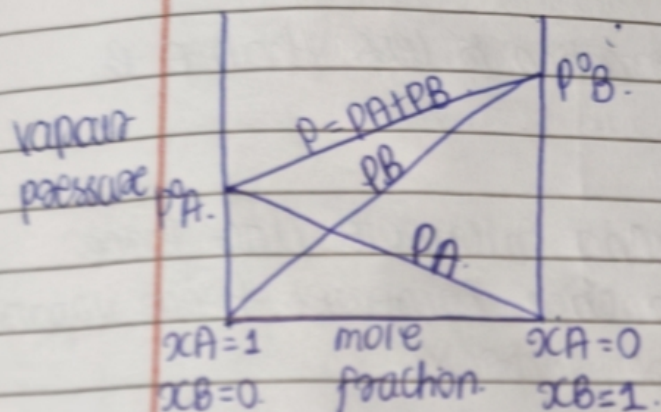
that is, interaction b/w A-B is the same as A-A and B-B:

(a) $\Delta H_{mix} = 0$

(b) $\Delta V_{mix} = 0$

(net endothermic or exothermic)

★ SOLUTIONS WITH SIMILAR FUNCTIONAL GROUPS ARE IDEAL.
eg:- benzene and toluene, chlorobenzene and bromobenzene.



★ Non Ideal Solution: is a soln that does not obey Raoult's law at all temperature and concentration.

① +ve deviation of Raoult's law:-

$A-A = B-B > A-B$, A-A and B-B transitions are greater than A-B interaction.

$$P_A > P^{\circ}_A \cdot x_A$$

$$P_B > P^{\circ}_B \cdot x_B$$

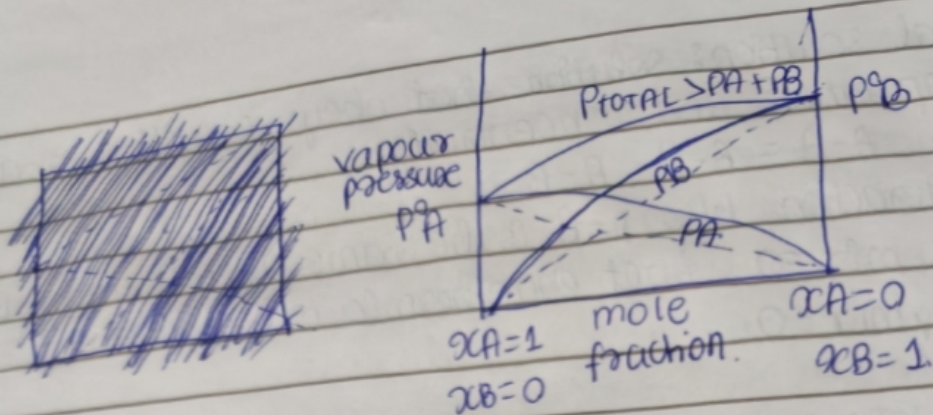
$$P_{total} > P_A + P_B$$

After mixing intermolecular force of attraction reduces and vapour pressure increases.

② $\Delta H_{mix} = +ve$ (endothermic reaction)

③ $\Delta V_{mix} = +ve$

eg: acetone and ethanol, C_2H_5OH and water.



⑤ Negative deviation from Raoult's law:-

$A-A = B-B < A-B$
 $A-A$ interaction and $B-B$ interaction is less than $A-B$ interaction.

$$P_A < P_A^0 \cdot x_A$$

$$P_B < P_B^0 \cdot x_B$$

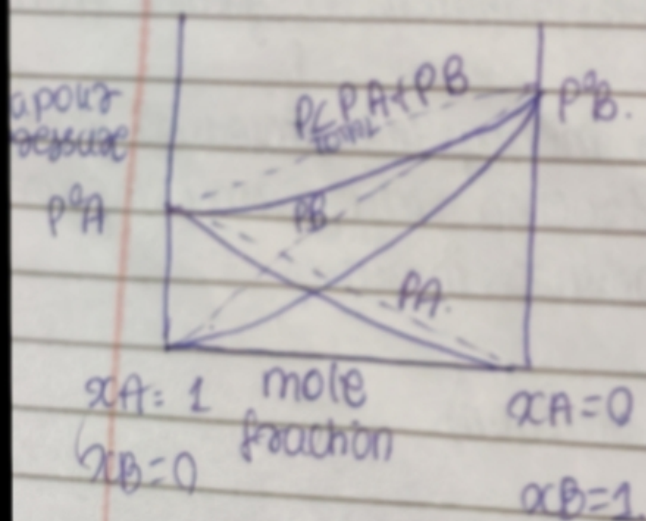
$$P_{TOTAL} < P_A + P_B$$

On mixing intermolecular force of attraction increases hence vapour pressure decreases

① $\Delta_{Hmix} = -ve$ (exothermic reaction)

② $\Delta_{vmix} = -ve$

eg: $HCl + H_2O$, acetone + aniline.



AZEOTROPES : mixtures of non-ideal solutions where both components vapourize and boil at the same temperature, also called constant boiling mixture.

① **Minimum Azeotropes** (+ve deviations of Raoult's law)

$$A-A \hat{=} B-B > A-B$$

① $\Delta H_{mix} = +ve$

② $\Delta V_{mix} = +ve$

more vapour pressure

eg: $CH_3COOH + C_6H_5OH$ and $C_6H_6 + CH_3COOH$

A solution at azeotropic composition will have boiling points less than the boiling points of individual components.

$$B.o.P_A + B.o.P_B > B.o.P_{A-B}$$

② **Maximum Azeotropes** (-ve deviation of Raoult's law)

$$A-A = B-B < A-B$$

① $\Delta H_{mix} = -ve$

② $\Delta V_{mix} = -ve$

min vapour pressure.

eg: $H_2SO_4 + H_2O$ and $HCl + NH_3$

A solution at azeotropic composition will have boiling point more than the boiling points of individual components.

$$B.o.P_A + B.o.P_B < B.o.P_{A-B}$$

COLLIGATIVE PROPERTIES [SOLID - LIQUID SOLUTION]

DEPEND ONLY ON NUMBER OF SOLUTE PARTICLES
NOT ON NATURE OF PARTICLES.

AS NO OF PARTICLES $\uparrow$:-

$\uparrow$ [VP $\uparrow$]
 $\uparrow$ [b.p.]

① vapour pressure and freezing point $\uparrow$
② boiling point and osmotic pressure $\uparrow$

- When volatile soln is added to solvent, $\text{vap} \uparrow$
 → When non-volatile soln is added to solvent, $\text{vap} \downarrow$.

(I) Relative lowering of VAPOUR PRESSURE.

vapour pressure: pressure exerted by the vapours of a liquid on its surface when the liquid and vapour are in equilibrium with each other at constant temperature.
 [vap changes due to shift in eqm. to regain its eqm. vap decreases]

p - vapour pressure of soln, p° - vapour pressure of solvent.

lowering of vapour pressure = $p^\circ - p$.

Relative lowering of vapour pressure = $\frac{p^\circ - p}{p^\circ}$

$$\frac{p^\circ - p}{p^\circ} \rightarrow \frac{n_B}{n_A + n_B} = \frac{p^\circ - p}{p^\circ}$$

★ RAOULTS LAW for relative lowering of vapour pressure
 The relative lowering of a non volatile solute dissolved in a solvent is equal to the mole fraction of the solute.

$$\frac{w_B \cdot M_A}{M_B \cdot w_A} = \frac{p^\circ - p}{p^\circ} \quad \left. \begin{array}{l} \text{mostly used in} \\ \text{numericals.} \end{array} \right\}$$

For a very dilute soln:

$$n_A + n_B \approx n_A$$

$$\frac{p^\circ - p}{p^\circ} = \frac{w_B \cdot M_A}{M_B \cdot w_A}$$

(II) OSMOTIC PRESSURE:

osmosis - flow of liquid from an area of higher concentration to a area of lower concentration through a semi permeable membrane.

example of :- natural spm :- cell membrane, protoplasm, animal bladder, membrane.
chemical spm :- visking tubing, dialysis membrane, cellophane, parchment paper.

osmotic pressure :- minimum pressure applied on the soln to prevent the entry of solvent molecules in the soln through a semi permeable membrane.

Reverse Osmosis :- When the pressure applied on the solution is greater than the osmotic pressure, the solvent starts flowing from solution into the solvent.

VANT HOFF'S BOYLES LAW :- At constant temperature osmotic pressure (π) of dilute solution is directly proportional to concentration

$$\pi \propto C$$

VANT HOFF'S CHARLES LAW :- At constant concentration osmotic pressure (π) of dilute solution is directly proportional to temperature

$$\pi \propto T$$

Combining both laws: $\pi \propto TC$ • ~~$\pi \propto TC$~~

$$C = \frac{W/M}{V}$$

$$\pi = RTC$$

$$\boxed{\pi = \frac{RTW}{MV}}$$

- ① isotonic solution: solution having the same osmotic pressure.
- ② hypotonic solution: solution whose osmotic pressure is less than that of another solution (compared to the cell)
eg: → water enters the cell → cell swells or bursts
- ③ hypertonic solution: solution whose osmotic pressure is higher than that of another solution (usually compared to cell)
eg: → water leaves the cell → cell shrinks.

★

DIFFUSION :	OSMOTIC DIFFUSION
• movement of solute molecules, no membrane needed	• movement of solvent molecules through semipermeable membrane
• solute molecules moves from high conc to low conc.	• solvent molecules moves through membrane from low conc to high conc.
• Flow of particles occurs in all the directions.	• Flow of particles occurs only in one direction.

(II) Depression in FREEZING POINT:

freezing point → is the temp at which solid and liquid state coexist.

(ve) Depression in freezing point: difference b/w the freezing point of pure solvent and freezing point of solution

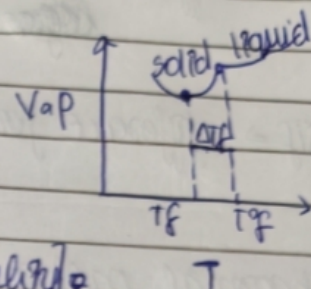
$$\Delta T_f = T_f - T_f'$$

* RAOULTS LAW for depression in freezing point when a non volatile solute is dissolved in solvent is directly proportional to molality of solution.

$$\Delta T_f = T_f^\circ - T_f$$

$$\Delta T_f = K_f \cdot m$$

$$\Delta T_f = K_f \cdot \frac{W_B \times 1000}{M_B \times W_A}$$



[When density is not given molality is equal to molarity]

$K_f \rightarrow$ molal depression constant OR CRYOSCOPIC CONSTANT.

definition of molal constant: depression in freezing point when: 1 mole of non-volatile solute is dissolved in 1 kg of solvent, kg/mol

(IV)

Elevation in boiling point: difference b/w point of soln and pure solvent when a non volatile solute is dissolved in a solvent.

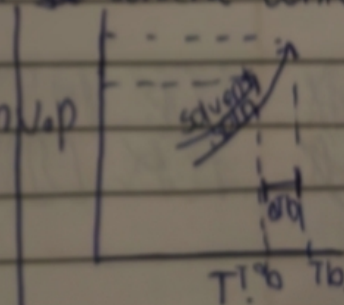
B.P $\rightarrow$ temp at which the vapour pressure of a liquid becomes equal to atmospheric pressure at boiling point

$$\Delta T_b = T_b - T_b^\circ$$

* RAOULTS LAW for elevation point in boiling point when a non volatile solute is dissolved in a solvent which is directly proportional to molality.

$$\Delta T_b = T_b - T_b^\circ \Rightarrow \Delta T_b = K_b \cdot m$$

$$\Delta T_b = K_b \cdot \frac{W_B \times 1000}{M_B \times W_A}$$



$\rightarrow$ BOILING POINT SCOPIC CONSTANT, $M_B \cdot W_A$

$K_b \rightarrow$ elevation of boiling point when one mole of solute is dissolved in 1 kg solvent, kg/mol.

DIFFERENCES:

* $\Delta T_b \rightarrow$ difference for boiling point -
 $\Delta T_b = T_b - T_b^\circ$

$K_b \rightarrow$ ebullioscopic constant

* $\Delta T_f \rightarrow$ difference for freezing point
 $\Delta T_f = T_f^\circ - T_f$

$K_f \rightarrow$ cryoscopic constant

Abnormal molar mass:-

* Due to association - no. of solute particles $\downarrow$,
 colligative properties $\downarrow$
 molar mass $\uparrow$

* Due to dissociation - no. of solute particles $\uparrow$,
 colligative properties $\uparrow$
 molar mass $\downarrow$

* Degree of association $\rightarrow$ fraction of total no. of molecules which associate.

$$\alpha = \frac{l-1}{n-1}$$

* Degree of dissociation $\rightarrow$ fraction of total no. of molecules which dissociate.

$$\alpha = \frac{l-1}{n-1}$$

* FOR ASSOCIATION $l < 1$
 * FOR DISSOCIATION $l > 1$

VANT HOFF'S FACTOR (i)

$$i = \frac{\text{actual molar mass}}{\text{observed molar mass.}}$$

(i) Relative Lowering of VAPOUR PRESSURE;

$$\frac{p^0 - p}{p^0} = i \times \frac{W_B \times 1000}{W_A \times M_B}$$

(ii) OSMOTIC PRESSURE;

$$\pi = \frac{C \cdot R T}{M}$$

(iii) Depression in FREEZING POINT.

$$\Delta T_f = i \cdot K_f \cdot \frac{W_B \times 1000}{M_B \times W_A}$$

(iv) Elevation of BOILING POINT.

$$\Delta T_b = i \cdot K_b \cdot \frac{W_B \times 1000}{M_B \times W_A}$$